DESCRIPTIONS OF HYDROGEN-OXYGEN CHEMICAL KINETICS FOR CHEMICAL PROPULSION

By
Forman A. Williams
Center for Energy Research
Department of Mechanical and Aerospace Engineering
University of California, San Diego
La Jolla, CA 92093-0411

There are many propulsion applications for which hydrogen and oxygen are attractive as fuel and oxidizer. These include liquid-propellant rocket motors with high specific impulse, air-breathing ramjets with supersonic combustion and certain types of pulse-detonation engines. Detailed knowledge of the chemical kinetics of combustion of hydrogen and oxygen is needed for rational design of combustors for such applications. Since there are only twenty-some steps in hydrogen-oxygen combustion chemistry, it is possible to ascertain all of the relevant rate parameters for this system much more accurately than for other fuel-oxidizer combinations. Although the relevant rate parameters are now rather well known, there are still some notable uncertainties that deserve further investigation. These include the falloff behavior at high pressures and chaperon efficiencies of various third bodies. More than twenty different mechanisms are currently available in the literature, some quite new. Predictions of these different mechanisms are in good agreement for most processes. There are, however, notable differences in predictions of autoignition induction times near crossover, where the rate of $H + O_2 \rightarrow OH + O$ equals the rate of $H + O_2 + M \rightarrow HO_2 + M$. Even certain very recent mechanisms are in poor agreement with experiment in this respect. A mechanism is given here that agrees well with experiment. A very simple mechanism consisting of only six irreversible elementary steps actually provides excellent agreement for autoignition delays over a very wide range of conditions. Simplifications of this type can be useful in computational fluid dynamics of reacting flows and in various practical propulsion calculations.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **22 JUN 2004**	2. REPORT TYPE **N/A**	3. DATES COVERED **-**
4. TITLE AND SUBTITLE **Descriptions Of Hydrogen-Oxygen Chemical Kinetics For Chemical Propulsion**		5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)		5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Center for Energy Research Department of Mechanical and Aerospace Engineering University of California, San Diego La Jolla, CA 92093-0411**		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES
See also ADM001793, International Symposium on Energy Conversion Fundamentals Held in Istanbul, Turkey on 21-25 June 2005.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**UU**	**12**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

DESCRIPTIONS OF HYDROGEN-OXYGEN CHEMICAL KINETICS FOR CHEMICAL PROPULSION

by

Forman A. Williams

Center for Energy Research

Department of Mechanical and Aerospace Engineering

University of California, San Diego

La Jolla, CA 92093-0411

International Symposium on Energy Conversion Fundamentals

Technical University of Istanbul, Turkey

June 22, 2004

Research Sponsored by AFOSR

PRACTICAL NEEDS

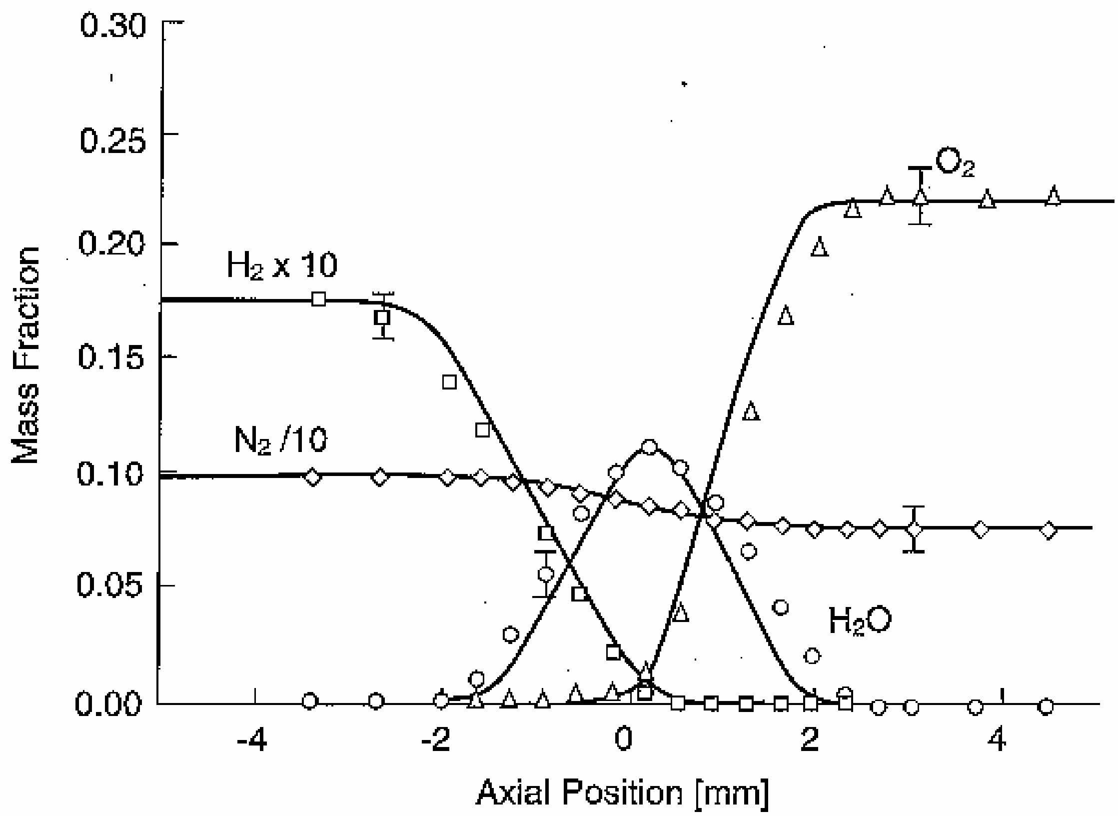
- Hydrogen-Oxygen Liquid-Propellant Rocket-Engine Chamber Volume
- Acoustic Instability in Liquid-Propellant Rockets
- Liquid-Propellant Rocket Throttling, Ignition and Extinction
- Hydrogen-Fueled SCRAMjet Autoignition
- Hydrogen-Fueled Airbreathing-Engine Flameout
- Pulse-Detonation Engines in Hydrogen-Oxygen or Hydrogen-Air Systems

EXPERIMENTAL TESTING GROUNDS FOR MECHANISMS

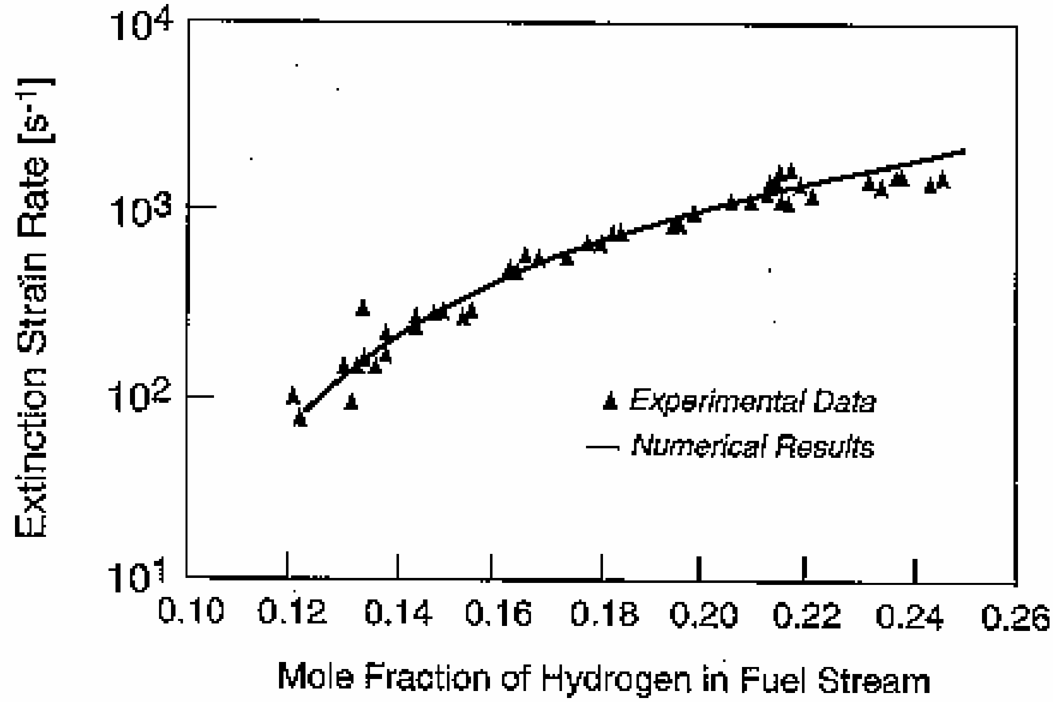
- Laminar Burning Velocities of Premixed Flames
- Structures of Premixed Laminar Flames
- Structures of Laminar Diffusion Flames
- Structures of Partially Premixed Laminar Diffusion Flames
- Extinction of Laminar Diffusion Flames
- Homogeneous Autoignition Times
- Ignition of Laminar Diffusion Flames
- Detonation Structures

PROBLEMS AND CONDITIONS OF INTEREST

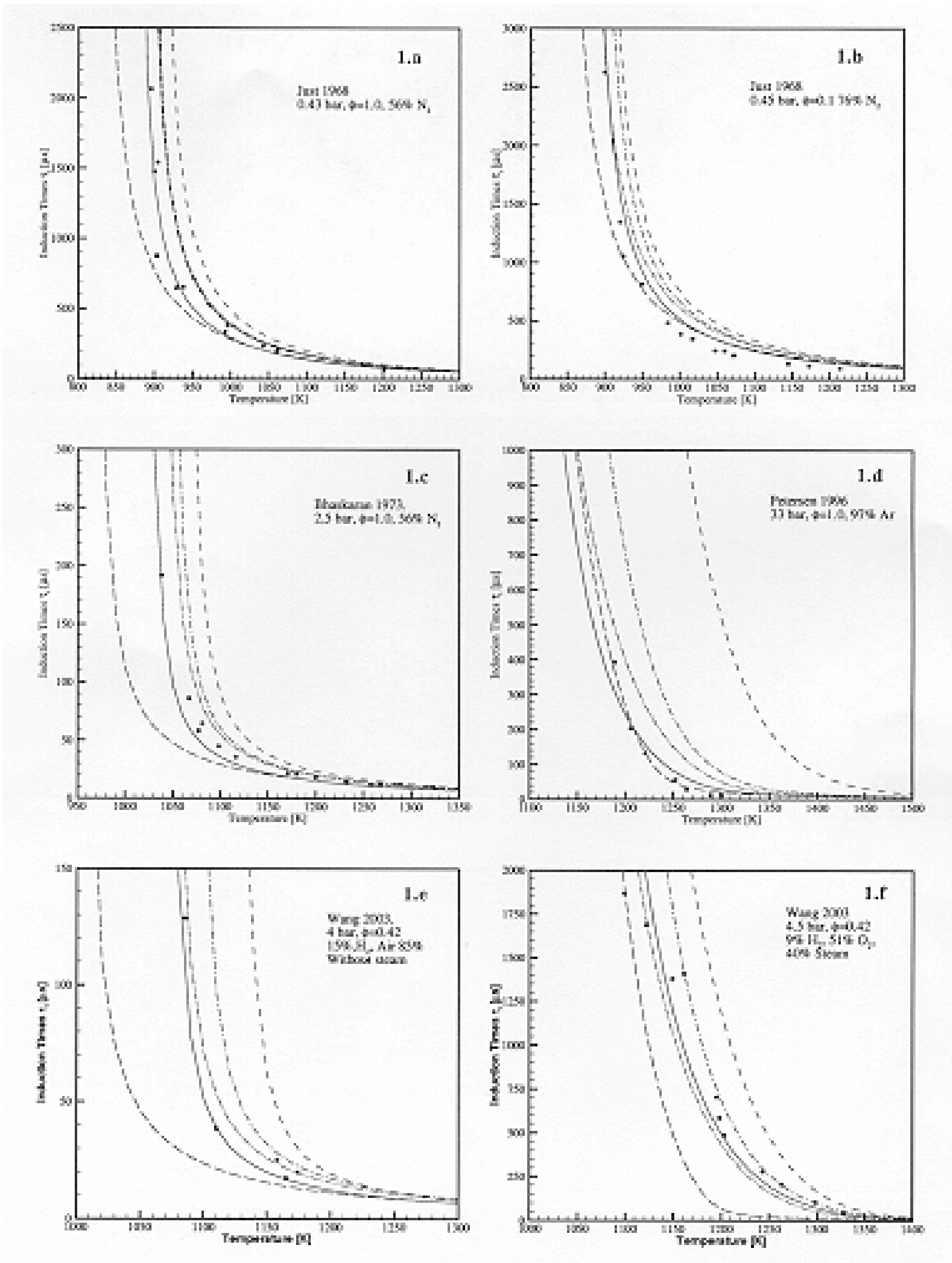
- Mainly Temperatures Above About 1000K, Pressures Below About 800 Bar and Equivalence Rations Less Than About 3
- Autoignition Times
- Extinction Conditions
- Acoustic Response Functions



0.30
0.25
0.20
0.15
0.10
0.05
0.00
Mass Fraction
H_2 x 10
N_2 /10
O_2
H_2O
-4
-2
0
2
4
Axial Position [mm]



Extinction Strain Rate [s-1]
Mole Fraction of Hydrogen in Fuel Stream
Experimental Data
Numerical Results
10^4
10^3
10^2
10^1
0.10
0.12
0.14
0.16
0.18
0.20
0.22
0.24
0.26



Comparisons of predictions of autoignition times for different chemical-kinetic mechanisms.

Number	Reaction		A^a	n^a	E^a
1	$H + O_2 \rightleftharpoons OH + O$		3.52E+16	-0.7	71.42
2	$H_2 + O \rightleftharpoons OH + H$		5.06E+04	2.67	26.32
3	$H_2 + OH \rightleftharpoons H_2O + H$		1.17E+09	1.3	15.21
4	$H_2O + O \rightleftharpoons OH + OH$		7.60E+00	3.84	53.47
5[b]	$H + O + M \rightleftharpoons OH + M$		6.20E+16	-0.6	0
6	$H_2 + O_2 \rightleftharpoons OH + OH$		1.70E+13	0	200.05
7[c]	$H + H + M \rightleftharpoons H_2 + M$		7.20E+17	-1	0
8[b]	$H + OH + M \rightleftharpoons H_2O + M$		2.20E+22	-2	0
9[b]	$O + O + M \rightleftharpoons O_2 + M$		6.17E+15	-0.5	0
10[d]	$H + O_2 + M \rightleftharpoons HO_2 + M$	k_0	2.60E+19	-1.2	0
		k_∞	4.65E+12	0.44	0
11[e]	$O + OH + M \rightleftharpoons HO_2 + M$		1.00E+16	0	0
12	$HO_2 + H \rightleftharpoons OH + OH$		1.70E+14	0	3.66
13	$HO_2 + H \rightleftharpoons H_2 + O_2$		4.28E+13	0	5.9
14	$HO_2 + H \rightleftharpoons H_2O + O$		3.10E+13	0	7.2
15	$HO_2 + O \rightleftharpoons OH + O_2$		2.00E+13	0	0
16	$HO_2 + OH \rightleftharpoons H_2O + O_2$		2.89E+13	0	-2.08
17[f]	$OH + OH + M \rightleftharpoons H_2O_2 + M$	k_0	2.30E+18	-0.9	-7.12
		k_∞	7.40E+13	-0.37	0
18	$HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2$		3.02E+12	0	5.8
19	$H_2O_2 + H \rightleftharpoons HO_2 + H_2$		4.79E+13	0	33.3
20	$H_2O_2 + H \rightleftharpoons H_2O + OH$		1.00E+13	0	15
21	$H_2O_2 + OH \rightleftharpoons H_2O + HO_2$		7.08E+12	0	6
22	$H_2O_2 + O \rightleftharpoons HO_2 + OH$		9.63E+06	2	16.7

The detailed mechanism with rate coefficients in the form $k=AT^n\exp(-E/RT)$.

[a] Units are mol,s,cm^3,kJ and K.

[b] chaperon efficiencies are 2.5 for H_2, 12.0 for H_2O, 1.9 for CO, 3.8 for CO_2 and 1.0 for all other species.

[c] chaperon efficiencies are 2.5 for H_2, 16.3 for H_2O, 1.9 for CO, 3.8 for CO_2 and 1.0 for all other species.

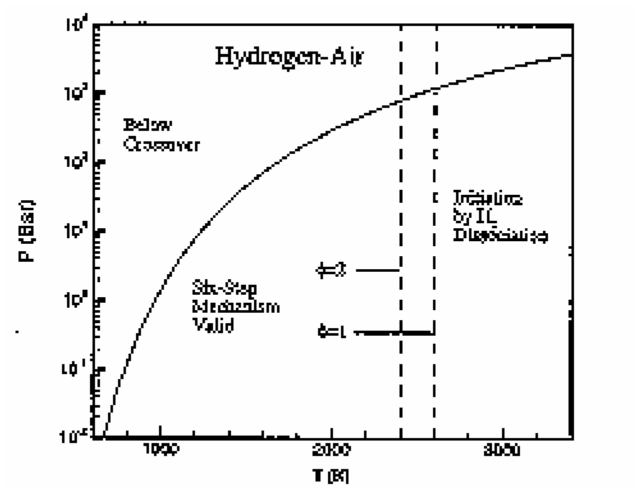
[d] chaperon efficiencies are 0.5 for Ar, 0.3 for O_2, 12.0 for H_2O, 0.75 for CO, 2.0 for CO_2, 3.0 for C_2H_6 and 1.0 for all other species; fall-off by the Troe formulation with $F_c = \exp(-T/345K) + \exp(-345K/T)$ (Troe, 2001).

[e] chaperon efficiencies are 1.0 for all species.

[f] chaperon efficiencies are 0.7 for Ar, 2.0 for H_2, 6.0 for H_2O, 1.5 for CO, 2.0 for CO_2, 2.0 for CH_4, 3.0 for C_2H_6 and 1.0 for all other species; fall-off by the Troe formulation with $F_c = 0.265\exp(-T/94K) + 0.735\exp(-T/1756K) + \exp(-5182K/T)$ (Petersen and Hanson, 1999).

Number	Reaction	Step in Table 2
1	$H_2 + O_2 \rightarrow OH + OH$	step 6 forward
2	$H_2 + O_2 \rightarrow HO_2 + H$	step 13 backward
3	$H + O_2 \rightarrow OH + O$	step 1 forward
4	$H_2 + O \rightarrow OH + H$	step 2 forward
5	$H_2 + OH \rightarrow H_2O + H$	step 3 forward
6	$H + O_2 + M \rightarrow HO_2 + M$	step 10 forward

The six-step mechanism for autoigntion.



Range of validity of the six-step short mechanism for autoignition. At crossover the rates of $H + O_2 \rightarrow OH + O$ and $H + O_2 + M \rightarrow HO_2 + M$ are equal.

CONCLUSIONS

- Good 22-step detailed mechanisms exist.
- At high pressures ($\geq$ 50 bar) it becomes important to include falloff, especially for $2OH + M \rightarrow H_2O_2 + M$.
- Chaperon efficiencies of water for $H + O_2 + M \rightarrow HO_2 + M$ have been improved recently.
- Most important uncertainties currently pertain to chaperon efficiencies.
- Most mechanisms give good results over rather wide ranges of conditions.
- Differences in predictions of different mechanisms are greatest for autoigntion near crossover.
- Even some of the new mechanisms in the literature are poor for autoignition near crossover.
- A simple irreversible six-step mechanism is good for predicting autoignition delays over a wide range of conditions.